

11.6: Phase Distribution Equilibria

Learning Objectives

- Phase distribution equilibria play an important role in chemical separation processes on both laboratory and industrial scales. They are also involved in the movement of chemicals between different parts of the environment, and in the bioconcentration of pollutants in the food chain.

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One's first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble.

For a solute S distributed between two phases a and b the process $S_a = S_b$ is defined by the distribution law

$$K_{a,b} = \frac{[S]_a}{[S]_b} \quad (11.6.1)$$

in which

- $K_{a,b}$ is the *distribution ratio* (also called the distribution coefficient) and
- $[S]_i$ is the solubility of the solute in the phase.

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-like substances; this is basically the mechanism whereby such residues as DDT can undergo *biomagnification* as they become more concentrated at higher levels within the food chain. For this reason, environmental regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard "oil" phase that is almost universally used is octanol, $C_8H_{17}OH$.

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a separatory funnel as shown below. The two immiscible liquids are poured into the funnel through the opening at the top. The funnel is then shaken to bring the two phases into intimate contact, and then set aside to allow the two liquids to separate into layers, which are then separated by allowing the more dense liquid to exit through the stopcock at the bottom.



If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the Le Chatelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.



Video 11.6.1: How to perform a liquid-liquid extraction using a separating funnel.

✓ Example 11.6.1

The distribution ratio for iodine between water and carbon disulfide is 650. Calculate the concentration of I_2 remaining in the aqueous phase after 50.0 mL of 0.10M I_2 in water is shaken with 10.0 mL of CS_2 .

Solution

The equilibrium constant is

$$K_d = \frac{C_{CS_2}}{C_{H_2O}} = 650$$

mmol, so $m_2 = (5.00 - m_1)$ mmol and we now have only the single unknown m_1 . The equilibrium constant then becomes

$$((5.00 - m_1) \text{ mmol} / 10 \text{ mL}) \div (m_1 \text{ mmol} / 50 \text{ mL}) = 650$$

Simplifying and solving for m_1 yields

$$\frac{(0.50 - 0.1)m_1}{(0.02m_1)} = 650$$

with $m_1 = 0.0382$ mmol.

The concentration of solute in the water layer is $(0.0382 \text{ mmol}) / (50 \text{ mL}) = \mathbf{0.000763 \text{ M}}$, showing that almost all of the iodine has moved into the CS_2 layer.

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